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THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF ORTHO AND META BROMO ANILINES IN VAPOUR PHASE

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(*Received November* 13, 1967; *Resubmitted July* 15, 1968)

(Plate 11)

ABSTRACT. The near ultraviolet absorption spectra of ortho and meta bromo anilines have been photographed in the vapour phase. A fairly intense band system analogous to the benzene forbidden transition could be identified in the region 3100A-2650A. From the analysis of the spectra, a number of excited state frequencies and also ground state frequencies could be established. From a comparative study of the spectra with other halogenated anilines and a few dihalogenated benzenes, probable modes of vibrations are also suggested.

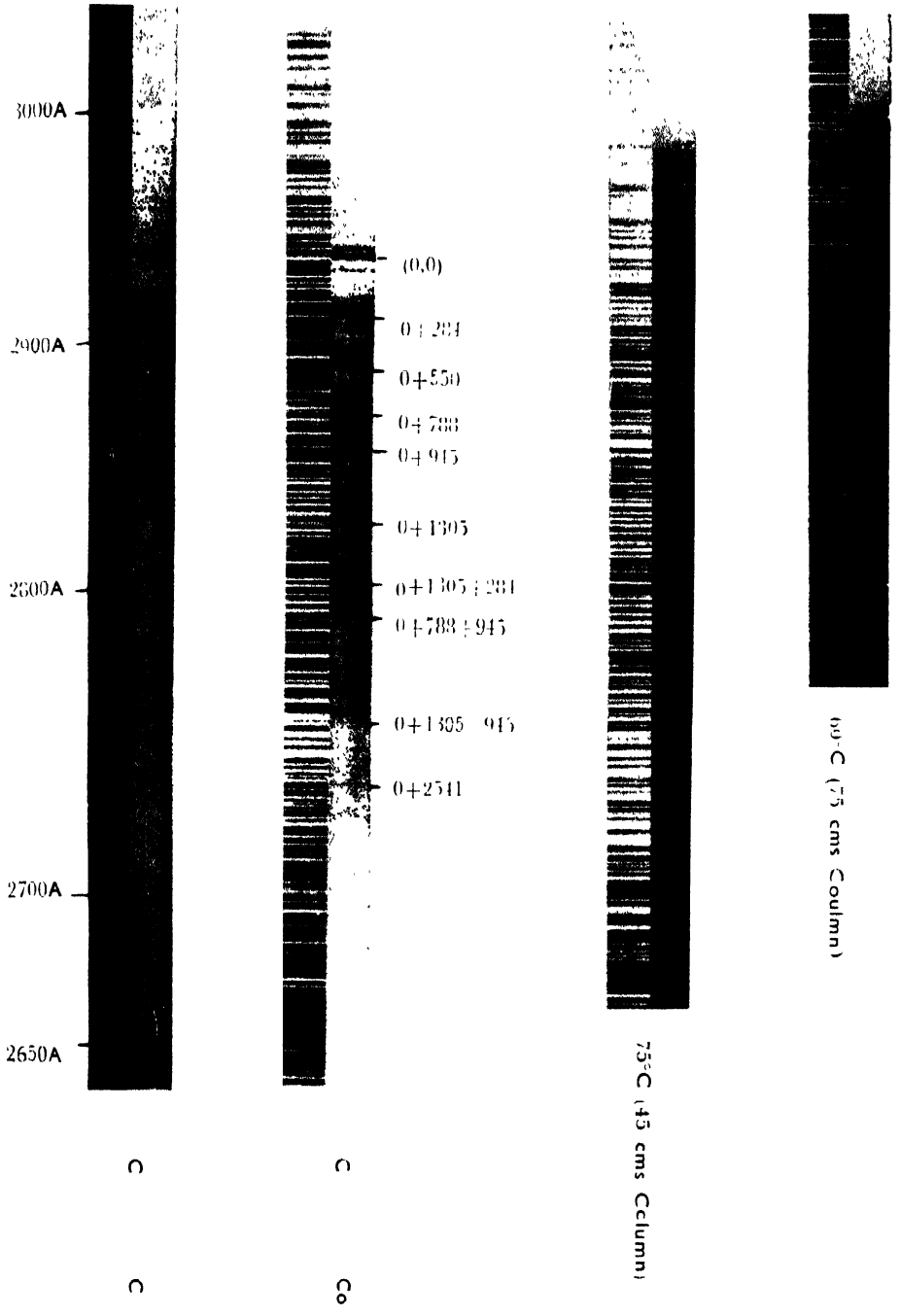
INTRODUCTION

The halogenated anilines are found to give rise to a discrete and fairly intense band system in the region of benzene forbidden electronic transition. Among the substituted anilines, the ultraviolet absorption spectra of the three isomeric fluoro anilines, (Murty and Santhamma, 1965; Shashidhar and Suryanarayana Rao, 1965) chloro anilines (Haranath and Sreerama Murty, 1957) and of *p*-bromo aniline (Sharma and Tripathi, 1964) are so far investigated in the vapour phase. The present investigation has been taken up with a view (1) to photograph the near ultraviolet absorption spectra of the other two isomers of bromo aniline to facilitate a comparison of the three isomers of chloro, fluoro and bromo anilines and certain dihalogenated benzenes (Krishnamachari, 1956) and (2) to establish, as far as possible the ground and excited state frequencies from a comprehensive comparison in the case of various isomeric halogenated anilines as these molecules are expected to give rise to similar frequencies characteristic of benzene ring and substituents.

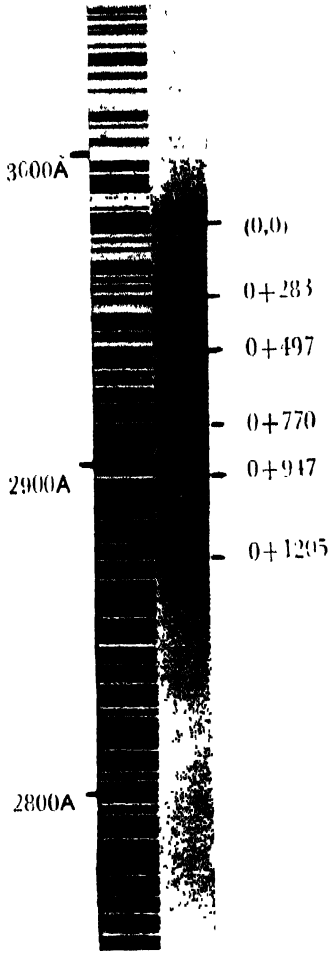
EXPERIMENTAL

The absorption spectra of a *o*-bromoaniline and *m*-bromo aniline have been recorded on Hilger quartz Spectrograph in the vapour state using two different columns (45 cms and 75 cms) of vapour for the ortho compound and one column (75 cms) for the meta compound.

Indian Journal of Phyics.
Vol.42 No 6
PLATE IIA



Indian Journal of Physics.
Vol. 42 No. 6
PLATE IIB



o-Bromo aniline

The spectrum of the ortho compound in the vapour phase is found to exhibit a very intense and well defined band system in the region λ3100A—2650A. The spectra are recorded at various temperatures ranging from —10°C to 90°C using a vapour column of 45 cms. The spectra are also recorded using a longer vapour column of 75 cms in the temperature range 29° to 70°C. Some of the very strong bands show a very clear red degradation. Using a vapour column of 75 cms at different temperatures, the molecule is found to exhibit a total absorption below λ2980A and with not much additional extension of the red and of the spectrum. The spectra recorded with two different vapour columns are given in plate 11A. Altogether about 70 bands could be measured on the Hilger comparator. The wave numbers of the band heads together with visual extimates of the intensities are given in table 1.

m-Bromo aniline

The spectrum of the meta compound using 75 cms of vapour column at different temperatures ranging from —10°C to 110°C, has given a fairly intense and discrete band system consisting of about 22 bands, in the region λ3000A–2800A. Band heads are measured under the Hilger comparator and the wavenumbers together with the visual estimates of intensity are given in the table 2. The spectrum recorded at 75°C wherein the maximum number of bands are measured is reproduced in the plate 11B.

ANALYSIS AND DISCUSSION

o-Bromo aniline. The molecule is of C_s point group symmetry and the characteristic features of the spectrum are in spport of this C_s symmetry. The 30 normal modes of vibration of this molecule (Taking NH_2 as a unit) are either of totally symmetric (a') or of non-totally symmetric (a'').

If the origin of the electronic transition is fixed at ν34052 cm^{-1}, this being the strongest band on the red end of the spectrum that could be recorded at —10°C using a vapour column of 45 cms., the bands could be well analysed in terms of twelve fundamental frequencies, 248, 284, 350, 486, 550, 750, 788, 945, 1173, 1305, 2541 and 2739 belonging to the upper electronic state of the molecule and seven frequencies 248, 289, 436, 468, 650, 650, 845 and 953 of the lower electronic state of the molecule. A few strong bands could also be given an alternative probable interpretation. This feature is not uncommon in molecules possessing C_s symmetry and a large number of atoms. The bands could be interpreted either as combinations of the fundamentals or overtones of the fundamentals or combinations with overtones as well. The alternative interpretations, where possible are also shown in the column under analysis of the table 1. A comparison of the excited state frequencies thus identified from the analysis of the spectrum of

this molecule with those established by previous workers in *o*-fluoro and *o*-chloro anilines and some other halogenated benzenes in the vapour phase has resulted in a probable assignment of the frequencies common to all these molecules.

284 cm^{-1}. The first very strong band giving rise to a frequency 248 cm^{-1} occurs also as a combination frequency. This frequency is not very prominently observed in *o*-fluoro and *o*-chloro anilines. This may probably represent a vibration wherein vibration of Br atom is involved.

284 cm^{-1}. An equally strong band at ν34336 cm^{-1} giving rise to the frequency 284 cm^{-1} occuring also as combinations with some of the other fundamental frequencies. This frequency may be considered to find its equivalence in *o*-fluoro aniline as 294, in *o*-chloro aniline as 261, and may be taken to represent a C- C-C plane bending mode in comparison with the frequencies established in some substituted halogenated benzenes

350 cm^{-1}. A strong band giving rise to a frequency 350 may be taken to represent an Eg^+ vibration of benzene in comparison with the similar frequency established in a few dihalogen substituted benzenes (Krishnamachari, 1956) and substituted anilines (Rama Rao and Santhamma, 1968). However this is not identified in *o*-fluoro aniline.

486 cm^{-1}. The frequency 486 occurs as combination with a few other fundamentals. Though the band giving rise to this frequency can also be interpreted as 2×248, yet it is preferred to be more a fundamental, as it is well comparable with the similar freequencies, 492 in aniline (Ginsburg and Matsen, 1945), 493 and 488 in *o*-and *m*-'chloro anilines 404, 447. and 422 in isomeric fluoro anilines, 418 and 472 in 2, 5 difluoro and 2, 5 dichloro anilines (Singh and Singh, 1965 and 1966) and 441 in 4Fl-3Cl aniline (Ramarao and Santhamma 1968). While this frequency is present in aniline and halogenated anilines it is totally absent in halogenated benzenes derived from the ultraviolet absorption spectra. As such one may probably interpret it as a vibration where the NH atoms take a prominent part. However, this range of frequency is also attributed to a C-C bending vibration.

550 cm^{-1}. This strong frequency falls in the region of C-Br stretching mode of vibration. A comparison of this frequency with the C-Br stretching frequencies identified in *o*-, *m*- and *p*-fluoro bromo benzene enables us to fix the frequencies 550 cm^{-1} in *o*-bromo aniline and 581 in *p*-bromoaniline as due to C-Br stretching mode of vibration. The probability of this region being one of the Eg^+ mode of vibration may not be considered, as generally such frequency is of less intensity than the lower component of the Eg^+ vibration.

750 cm^{-1}, 788 cm^{-1} and 945 cm^{-1}. This is the region where a totally symmetrical C-C frequency (ring breathing) or a totally symmetric trigonal bending frequency occur with strong intensity in these molecules in excited state. The frequencies 750 or 788 may be taken to represent a C-C ring breathing frequency

whereas the frequency 945 may be preferred to represent a C-C-C trigonal bending frequency. The corresponding ground state frequencies observed in ultraviolet absorption are 845 and 953 respectively. This assignment is in support of such a reduction of ring breathing frequencies even in the ground state in ortho and para compounds where one expects a much lowering of the ring breathing frequency of benzene upon ortho and para disubstitution (Pitzer and Scott, 1943). 945 cm^{-1} may represent a totally symmetric C-C frequency, probably a C-C-C trigonal bending which appears to have a higher frequency than the ring breathing frequency in ortho and para compounds (Krishnamachari, 1956).

1173 cm^{-1} and 1305 cm^{-1}. These fall in the region of C-H planar bending mode of vibration could be identified with fairly good intensity in a number of substituted benzenes for example 1134 and 1245 in *o*-fluoro aniline and 1300 in *o*-chloro aniline. 1076, 1023 in *o*-and *m*-fluoro chloro benzenes. 1042, 1001 in *m*- and *p*-fluoro bromo benzenes, 1034. 1069. 1075 and 1056 in the three isomers of chloro bromo benzenes, 1044 in 4Fl-3Cl aniline, 1072 and 1059 in 2. 5 difluoro and 2, 5 dichloro anilines

2541cm^{-1} and 2739 cm^{-1}. The two strong frequencies occur in the region of C-H stretching vibration and may be assigned as such.

GROUND STATE FREQUENCIES

From the ultraviolet absorption spectrum, the frequencies characteristic of the ground state of this molecule could also be identified. The two frequencies 248 and 289 fall in the region of C-C-C planar bending mode of vibration. 289 may be correlated with 284 observed in the excited state. The strong frequency 436 observed in the ground state of this molecule may correspond in the excited state to 350. 650 cm^{-1} in the ground state may represent a C-Br stretching mode of vibration the value of which in the excited state is identified as 550 cm^{-1}. The frequencies 953 and 845 in the ground state may be associated with the frequencies 945 and 788 or 750 in the excited state of the molecule respectively. 0-94 may be interpreted as the difference between 436 and 550 or 845 and 750.

ANALYSIS AND DISCUSSION

m-Bromo aniline. Fixing the origin of the electronic transition at 33579 cm^{-1} the bands towards the violet side could be interpreted in terms of frequencies 220, 283, 497, 770, 947, 1255 and 1307 characteristic of the excited state and the two frequencies 233 and 421 on the red side as the characteristic of the ground state of the molecule. The spectrum of *m*-bromo aniline is not very extensive and only a very few bands could be developed on the higher wavelength side of the origin.

A comparison of the frequencies identified in the present work in the ortho and meta compounds and the ones reported in para compound by Sharma and

Table 1

Frequency in wave number (cm^{-1})	Visual Intensity	Difference	Assignment
33053	w	999	0—953—57
33099	m.s	953	0—953
33207	m.s	845	0—845
33279	m.s	773	0—650—2×57
33365	m.s	687	0—436—248
33402	m.s	650	0—650
33518	m.s	534	0—248—289
33554	m.s	498	0—2×248, 0—436—57
33584	m.s	468	0—468
33616	s	436	0—436
33665	m.s	387	0—289—2×57
33714	m.s	338	0—289—57
33763	m.s	289	0—289
33804	v.s	248	0—248
33880	m.s	172	0—3×57
33936	m.s	116	0—2×57
33957	m.s	94	0—94
33995	v.s	57	0—57
34052	v.v.s	0	0,0
34143	s	91	0+91, 0+350—248
34216	m.s	164	0+350+91—284
34251	m.s	199	0+248—57, 0+486—284
34300	v.v.s	248	0+248
34336	v.v.s	284	0+284
34370	m.s	318	0+486—3×57
34402	v.s	350	0+350, 0+248+91
34442	m.s	390	0+550—3×57
34489	s	437	0+350+91, 0+486—57, 0+550—2×57
34538	v.s	486	0+486, 0+2×248, 0+550—57
34602	v.s	550	0+550
34757	s	705	0+2×350
34802	s	350	0+750
34840	s	788	0+788
34904	s	852	0+486+284+91, 0+750+91, 0+945—94
34953	m.s	901	0+350+550
34997	v.s	945	0+945

Table 1 (contd.)

Frequency in wave number (cm^{-1})	Visual Intensity	Difference	Assignment
35054	m.s	1002	0+750+248
35225	m.s	1173	0+1173
35286	s	1234	0+945+284
35357	v.s	1305	0+1305, 0+945+350
35487	v.s	1435	0+945+486
35551	s	1499	0+2×750, 0+945+550, 0+2×350+788
35603	s	1551	0+1305+248
35635	v.s	1583	0+2×788, 0+1305+284
35711	s	1659	0+1305+350, 0+1173+486
35749	s	1697	0+750+945
35795	v.s	1743	0+788+945
35861	v.s	1809	0+1173+550+91, 0+1305+2×248
35941	m.s	1889	0+2×945
36008	v.s	1956	0+788+1173
36095	m.s	2043	0+788+1173+91, 0+1305+750
36140	m.s	2088	0+788+1305
36175	m.s	2123	0+1173+945
36234	s	2182	0+2×945+284
36261	m.s	2209	0+1173+945+91
36309	s	2257	0+1305+945, 0+3×750, 0+2×945+284+91
36448	s	2396	0+1173+945+284
36510	m.s	2458	0+1173+945+350, 0+2×248+1173+788
36558	s	2506	0+1173+788+550
36593	v.s	2541	0+2541
36651	m.s	2599	0+2×1305
36695	s	2643	0+2541+91, 0+2×945+750
36743	m.s	2691	0+2×1305+91
36791	s	2739	0+2739
36848	m.s	2796	0+2541+248, 0+3×750+550, 0+2×945+550+350
36898	m.s	2846	0+3×945
37017	w	2965	0+2×1305+350
37059	w	3007	0+4×750
37092	m.s	3040	0+2541+788
37130	m.s	3078	0+2739+350

v.v.s=Very very strong, v.s.=Very strong, s=Strong, m.s=Medium strong, w=Weak.

Table 2

Frequency in wave number (cm^{-1}.)	Visual Intensity	Difference	Assignment
33158	m.s	421	0−421
33346	m.s	233	0−233
33542	s	37	0−37
33579	v.s	0	0, 0
33757	m.s	178	0+220−37
33799	m.s	220	0+220
33827	m.s	248	0+283−37
33862	v.s	283	0+283
34032	s	453	0+497−37
34076	v.s	497	0+497, 0+220+283
34349	v.s	770	0+770, 0+283+497
34414	s	835	0+1255−421
34466	m.s	887	0+1307−421
34526	v.s	947	0+947
34582	s	1003	0+2×497
34738	m.s	1159	0+1159, 0+947+220
34834	vls	1255	0+1255, 0+770+497
34886	m.s	1307	0+1307
34943	m.s	1364	0+1159+220
34998	m.s	1419	0+1159+283−37
35287	m.s	1708	0+947+770
35335	m.s	1756	0+1255+497

*V.s=Very strong, s=strong, m.s=Medium strong.

Table 3

o-Bromo aniline		*m*-Bromo aniline		*p*-Bromo aniline		Mode of vibration
Ground state	Excited State	Ground State	Excited State	Ground State	Excited State	
248		233				C-C-C Plane bending
	248		220			C-Br Planar bending ?
289	284		283	290	270 286	C-C-C Plane bending
436	350	421		397	360	E_g^+ vibration of benzene (Corresponding to 606 Cm^{-1} vibration of benzyne)
468						C-C bending
	486		497			C-NH involving or C-C bending
650	550			635	581	C-Br stretching
845	750 or 788		947	829	761	C-C Breathing
953	945		770			C-C-C (Trigonal bending)
	1173				1168	C-H Planar bending
			1255			
	1305		1307		1305	
	2541 2739					C-H stretching

Tripathi (1964), with those identified in a few dihalogenated benzenes and substituted anilines has enabled us to suggest a probable mode of vibration for the frequencies. A correlation of the frequencies identified in the three isomers of bromo anilines is given in the table 3.

ACKNOWLEDGMENTS

The author is indebted to Dr. (Mrs) C. Santhamma, under whose guidance this work has been carried out. He is also deeply indebted to Prof. K. R. Rao, Professor Emeritus, Andhra University, for his keen interest and inspring encouragement during the process of this work.

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